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Conducting charge-transfer salts based on neutral π-radicals

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MOST molecular conductors rely on charge transfer to create carriers. For example, the ET salts[1] are hole-doped whereas the C_{60} salts[2] are electron-doped. Neutral radical species in which bands are formed by π-orbital overlap would be expected to have half-filled bands and thus to be conducting[3], but no such metals have yet been reported. Here we report the synthesis and characterization of a molecular conductor which combines both of these approaches: energy bands are formed from one-dimensional stacks of neutral π-radicals, and the material is rendered conducting by electron transfer from the conduction band following doping with an acceptor. The radical species is the 1,4-phenylene-bis(dithiadiazolyl) diradical 1,4-[$(S_2N_2C)C_6H_4(CN_2S_2)$] (2 in Fig. 1), reaction of which with iodine vapour leads to crystals of [2][I]. At low temperatures this compound is essentially a diamagnetic insulator, but above 200 K the conductivity and magnetic susceptibility increase markedly, and at room temperature the conductivity reaches 100 S cm^{-1}, which is comparable to that shown by conventional molecular charge-transfer salts.

The preparation of synthetic conductors usually involves the oxidation or reduction of a closed-shell molecule to generate a mixed-valence or charge-transfer salt[1,2]. We have been interested in an alternative approach, namely the use of neutral π-radicals, in which the requirement for a partially filled energy band is inherently fulfilled[3]. There are, however, few π-radicals with sufficient stability and flexibility[4-6]. Initially we examined variants of the phenalenyl radical[7-10], but recent advances in heterocyclic chemistry have provided a variety of potentially useful π-radical building blocks[11,12]. One objective has been to generate

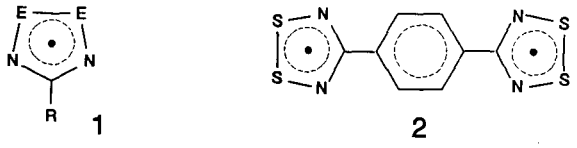

FIG. 1 The molecular structures of the neutral radical dithiadiazolyl (1), where E is S or Se, and the 1,4-phenylene-bis(dithiadiazolyl) diradical (2).

materials consisting of molecular stacks or columns, and for several choices of the R-group in 1 (Fig. 1, E = S, Se), this packing arrangement has been realized[11,13]. By definition, however, neutral radicals give rise to a half-filled electronic energy band, which in a one-dimensional packing arrangement is prone to a Peierls instability (essentially a dimerization process) driven by charge density waves (CDWs). Because the radicals tend to dimerize, we have attempted to stabilize the metallic state by applying pressure and by preparing materials in which two- and three-dimensional interactions are enhanced. Several small-band-gap semiconductors of this kind (with E = Se) have been characterized[11,13,15], but no truly metallic compound has yet been realized.

An alternative strategy for stabilizing the metallic state involves doping the energy band away from the half-filling which is characteristic of the neutral state. We have now found that the oxidation of the 1,4-phenylene-bridged bifunctional radical 2 (Fig. 1, ref. 14) with iodine produces a highly conductive mixed-valence salt of formula [2][I]. The preparation requires heating a mixture of 2 (1.0 mmol) and I_2 (0.5 mmol) in a sealed, evacuated (1 mTorr) pyrex tube (25 × 250 mm). Slow fractional sublimation along a temperature gradient (225 °C to 160 °C over 100 mm) affords, after several days, lustrous silver black needles with elemental composition $C_8H_4N_4S_4I$ (yield ~70%).

The crystal structure (Fig. 2) consists of columns of uniformly spaced (3.415(2) Å) molecules of 2 interspersed by columns of disordered iodines running along the *x*-axis. Perpendicular to the stacking direction the heterocyclic rings lie in dove-tailed arrays running parallel to the *y*-axis. Within the CN_2S_2 rings, the S–S (2.066(1) Å) and S–N (1.616(2) Å) bonds are between those seen in the neutral dimer of 2 (ref. 14) and its di-cation $[2]^{2+}$ (ref. 15), but closer to the former, implying an oxidation state (per ring) of <0.5.

The magnetic susceptibility of [2][I] was determined between 4 K and the decomposition point using the Faraday technique (Fig. 3). At low temperatures there is a small Curie tail due to

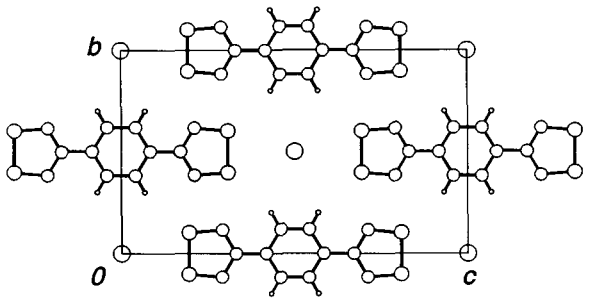

FIG. 2 The crystal structure of [1,4-(S_2N_2C)C_6H_4(CN_2S_2)][I]. The space group is orthorhombic *Immm* with (at 23 °C) a=3.415(2) Å, b=10.061(2) Å, c=16.740(2) Å, FW=411.31, Z=2. (Where FW is the formula weight, and Z is the number of molecules in the unit cell.) The crystals have a large mosaic spread, typically ~1°. The non-hydrogen coordinates are S, 0, 0.10269(5), 0.19337(3); N, 0, 0.11573(20), 0.28955(12); C1, 0, 0, 0.32886(19); C2, 0, 0, 0.41657(18); C3, 0, 0.11905(23), 0.45886(14). The iodine atoms are disordered along x. In the final room temperature refinement, (R-value, 0.027) the iodine positions were modelled by partial iodines at 0, 0, 0 (occupancy 0.472), ±0.225, 0, 0 (0.221) and 0.500, 0, 0 (0.104).

defects in the crystal. Above 180 K there is a steep rise in the paramagnetism, which becomes almost linear above room temperature. An electron spin resonance study of crystals of [2][I] showed the same rise in susceptibility, with a large increase in the linewidth from 20 G at 100 K to 130 G at room temperature. The g-value of 2.013 was about the same as that observed for 2 (ref. 14).

Single crystals of [2][I] were wired for four-point conductivity measurements along the stacking axis (x). Gold pads were first evaporated onto the crystals. Wires were attached to the pads with gold or silver paint, for experiments below or above room temperature, respectively. The conductivity (Fig. 4) is activated in the low temperature regime (<200 K), and there are two points of inflection between 170 and 210 K; the low-temperature transition shows hysteresis (inset). From 210 K until decomposition the conductivity is weakly metallic. The highest conductivity is attained at ~350 K where σ=100 S cm^{-1}. At a pressure of 1.5 GPa the conductivity is increased by a factor of about four, and the low-temperature phase transition is suppressed.

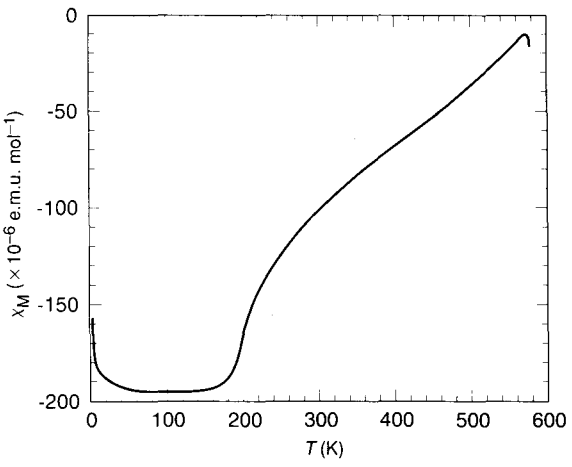

FIG. 3 The magnetic susceptibility of [2][I] as a function of temperature. A Curie–Weiss fit to the low-temperature data gave a spin concentration of 0.04% on a per-molecule basis and the diamagnetism was found to be −197 p.p.m. e.m.u. mol^{-1}. Based on earlier solid-state magnetic susceptibility studies on undoped 2 (ref. 14) and using Pascal's constants the measured diamagnetism is consistent with the molecular formula.

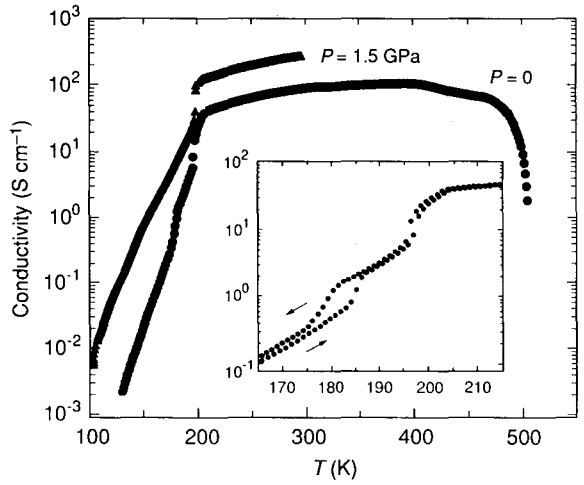

FIG. 4 The electrical conductivity of [2][I] as a function of temperature and applied pressure (P).

Low-temperature X-ray diffraction was performed on a single crystal of [2][I] using a Cu Kα rotating-anode X-ray source and a closed-cycle helium refrigerator. A singly-bent pyrolytic graphite monochromator and a flat graphite analyser were used to increase the signal-to-noise ratio and minimize scattering from the cryostat Be windows. This arrangement results in a symmetric resolution function with a resolution width of ~0.01 Å^{-1}. Because of the large mosaic spread in crystals of [2][I], scans in any direction but the radial direction are expected to show additional broadening from the mosaic structure of the crystal.

A search for a low temperature superlattice was undertaken by scanning parallel to [h00], the chain axis, at various points

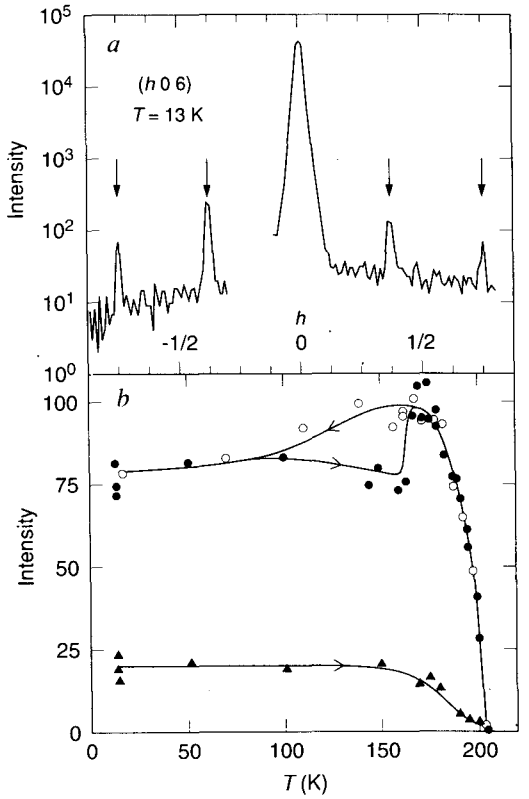

FIG. 5 *a*, Superlattice peaks observed for [2][I] along (h06) at 13 K. *b*, Temperature dependence of the superlattice reflections for [2][I]. Intensity is given in arbitrary units. Data for warming and cooling are shown by solid and open symbols respectively.

in reciprocal space. The results of scanning along [h06] are shown in Fig. 5a. Small superlattice peaks marked with arrows can be seen at $h = \pm 3\ 8$ and $h = \pm 6/8$ around the (006) Bragg reflection. The third harmonic at $h = 9/8$ was not observed, nor was the Bragg reflection at (106), which is absent because of the body-centred lattice. Similar superlattice peaks were observed around nearly every major Bragg reflection in the (0$k$$l$) zone, but were not observed around (00l) Bragg reflections.

The temperature dependence of the (3/8 0 6) and the (6/8 0 6) superlattice reflections are shown in Fig. 5b. The onset transition is near 200 K in agreement with the magnetic susceptibility and conductivity measurements and is taken as evidence of the formation of a CDW. The increase of the intensity of the (3/8 0 6) reflection below the phase transition is quite steep, but apparently second order. The increase of the intensity of the second-order superlattice peak below the transition is less steep, as is expected because its intensity should be proportional to the fourth power of the order parameter rather than the second power.

There is an anomalous 'bump' in the intensity of the first-order satellite near 170 K on warming and a gradual decrease of the order parameter below 170 K on cooling. There is some ambiguity in determining the intensity of an X-ray from a scan through a broad, mosaic peak, however similar hysteretic behaviour, with a smaller range of hysteresis, is seen in the conductivity. This could be the signature of an additional CDW phase transition, but a superlattice from a second CDW has not been seen. The CDW wavevector is apparently commensurate at $h = 3/8$ at all temperatures in the range 10–300 K, however the low q-resolution of this experiment may have failed to detect a region of incommensurability near the phase transition.

In a one-dimensional conductor the CDW wavevector gives the band-filling directly[16], and thus we infer three-eighth-full conduction band(s) in [2][I]. In our previous studies of neutral biradicals such as 2, the two dithiadiazolyl rings (1) were uncoupled and the biradicals could be treated as containing independent spin systems. If this argument is extended to [2][I] then every molecule of 2 is involved in two independent conduction bands each of which contains three-quarters of an electron per molecule for a net charge transfer of one-quarter of an electron per dithiadiazolyl ring to give $[2]^{1/2+}[I]^{1/2-}$. Alternatively, if there is a single conduction band which comprises both dithiadiazolyl rings, then the degree of charge transfer is one-half an electron on a per molecule basis from a conduction band which has a capacity of four electrons for the same overall division of charge. The iodines could consist of equal amounts of I^- and I_3^-.

The rise in the susceptibility is reminiscent of the behaviour shown by other neutral biradicals, particularly the 1,3-isomer of 2, which have shown giant paramagnetism[13]. The paramagnetism attained by [2][I] is much smaller and only corresponds to one-quarter of a spin per molecule on a Curie basis at the highest temperatures. The present case differs from that of the neutral biradicals in that the spins generated in [2][I] are itinerant and make a significant contribution to the conductivity. Interpreted as Pauli spins the highest value of the magnetic susceptibility corresponds to a density of states at the Fermi level, $n(E_f) \sim 6$ states (total) (eV mol)$^{-1}$, considerably larger than would be expected for a one-dimensional metal based on the dithiadiazolyl system 1, near half-band filling. Furthermore the increase in magnetic susceptibility with temperature above 200 K and the flat conductivity suggests that carriers are still being generated at these temperatures.

The period of the CDW found in [2][I] is of note in view of our previous work on neutral radical-based molecular conductors[11,13]. By definition the latter compounds give rise to a half-filled conduction band and in all cases we have found that the molecules are dimerized, except perhaps at high temperatures where magnetic excitations are detectable in some of the sulphur compounds[13]. Previously we have attempted to stabilize the metallic state and overcome the CDW in neutral radicals by using high pressure and by attempting to synthesize new systems with sufficient three-dimensional character to stabilize the Fermi surface against distortions. The present results suggest that doping the materials away from one-half to three-eighths band-filling also suppresses the formation of CDWs and is an effective route to conducting materials. The solid-state properties of [2][I] suggest that charge-transfer salts derived from neutral heterocyclic radicals represent a promising direction in the search for molecular electronic materials. □

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1. Williams, J. M. *et al. Organic Superconductors* (Prentice-Hall, Englewood Cliffs, 1992).
2. Haddon, R. C. *et al. Am. chem. Soc. Symp. Ser.* **481,** 71–89 (1992).
3. Haddon, R. C. *Nature* **256,** 394–396 (1975).
4. Soos, Z. G., Keller, H. J., Moroni, W. & Nothe, D. *Ann. N.Y. Acad. Sci.* **313,** 442–458 (1978).
5. Nakasuji, K. *et al. J. Am. chem. Soc.* **111,** 9265–9267 (1989).
6. Schultz, A. J. *et al. Inorg. Chem.* **26,** 3757–3761 (1987).
7. Haddon, R. C. *et al. J. Am. chem. Soc.* **100,** 7629–7633 (1978).
8. Haddon, R. C., Chichester, S. V., Stein, S. M., Marshall, J. H. & Mujsce, A. M. *J. org. Chem.* **52,** 711–712 (1987).
9. Oakley, R. T., Reed, R. W., Cordes, A. W., Craig, S. L. & Graham, J. B. *J. Am. chem. Soc.* **109,** 7745–7749 (1987).
10. Hayes, P. J., Oakley, R. T., Cordes, A. W. & Pennington, W. T. *J. Am. chem. Soc.* **107,** 1346–1351 (1985).
11. Cordes, A. W., Haddon, R. C. & Oakley, R. T. in *The Chemistry of Inorganic Ring Systems* (ed. Steudel, R.) 295–321 (Elsevier, Amsterdam, 1992).
12. Banister, A. J. & Rawson, J. M. in *The Chemistry of Inorganic Ring Systems* (ed. Steudel, R.) 323–348 (Elsevier, Amsterdam, 1992).
13. Andrews, M. P. *et al. J. Am. chem. Soc.* **113,** 3559–3568 (1991).
14. Cordes, A. W. *et al. J. Am. chem. Soc.* **113,** 582–588 (1991).
15. Liblong, S. W., Oakley, R. T. & Cordes, A. W. *Acta crystallogr.* C**46,** 140–142 (1990).
16. Torrance, J. B. *Ann. N.Y. Acad. Sci.* **313,** 210–233 (1978).

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